ligand trans to the oxo (1.654 (17) Å). Therefore, an average Tc=O bond length is taken to be 1.65 (2) Å. Complexes containing the *trans*-dioxotechnetium(V) core (entries 16–21) exhibit a fairly narrow range of Tc=O bond distances and the average of these, 1.74 (2) Å, can now be considered standard for this core. Technetium–oxygen single-bond distances exhibit considerable variation, which is sometimes due to partial double bonding, as is probable in [O(CH₃CH₂O)-Br₂(4-nitropyridine)₂Tc$^V$],[12] or steric strain, as in [TcO(pencil)₂]³¹ and [Tc(EDTA)]²⁺.³² Excluding these complexes, the

average Tc–O distance is 1.98 (3) Å. Bond lengths for Tc-(V)–N fall into a fairly wide range (2.00–2.35 Å), with the extremes resulting from chelate effects. The average of all Tc–N distances (2.14 (8) Å) is not appreciably different from that including only sterically unhindered nitrogen ligands (2.15 (1) Å for entries 15–18), which should be taken as the standard length.

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# Molecular and Electronic Structures of Two 16-Electron Complexes of Tungsten(II): WBr₂(CO)₂(C₇H₈) (C₇H₈ = Norbornadiene) and WBr₂(CO)₂(PPh₃)₂

F. A. COTTON* and J. H. MEADOWS

The previously reported reaction of WBr₂(CO)₄ with norbornadiene has been reinvestigated and found to give monomeric WBr₂(CO)₂(C₇H₈) (1). Compound 1 crystallizes from CH₂Cl₂ in the monoclinic space group *P*2₁/*n* with lattice dimensions *a* = 7.506 (7) Å, *b* = 12.643 (8) Å, *c* = 12.296 (6) Å, *β* = 99.60 (7)°, *V* = 1150 (2) Å³, and *Z* = 4. The structure was refined to $R_1$ = 0.032 and $R_2$ = 0.038. Compound 1 is a diamagnetic d⁴ complex having a pseudo-octahedral geometry with its CO ligands trans to each other. Compound 1 also has relatively short W–Br (2.493 (1) and 2.489 (1) Å) bond lengths. Another 16-electron d⁴ tungsten complex, WBr₂(CO)₂(PPh₃)₂ (2), was also structurally characterized. Compound 2 crystallizes in the triclinic space group *P*Ī with lattice dimensions *a* = 9.418 (5) Å, *b* = 10.021 (4) Å, *c* = 19.898 (6) Å, *α* = 90.54 (3)°, *β* = 112.80 (3)°, *γ* = 92.02 (4)°, *V* = 1730 (1) Å³, and *Z* = 2. The structure was refined to $R_1$ = 0.064 and $R_2$ = 0.072. Compound 2 has an overall geometry greatly distorted from octahedral. Fenske–Hall type molecular orbital calculations were performed on models of 1 and 2 to determine the principal factors responsible for the removal of t₂g orbital degeneracy. The calculational results predict a lowest energy allowed transition between orbitals separated by ca. 3 eV for both 1 and 2. This transition is assigned to visible transitions observed at 565 and 545 nm for 1 and 2, respectively. The calculations indicate that the LUMO–HOMO separation in 1 can be attributed to metal d to CO π* and olefin π* back-donation, which results in the lowering of two orbitals preferentially. In 2 it appears that the strong distortions from octahedral symmetry, especially the P–M–P angle of only 128°, are as important as π bonding in giving the singlet ground state.
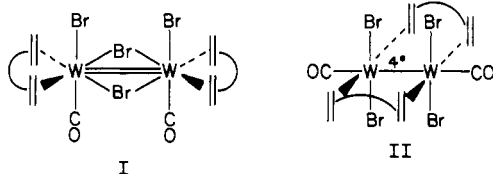
## Introduction

Work in this laboratory involving d⁴ transition-metal complexes has largely focused on the tendency of this electronic configuration to form multiple metal–metal bonds.[1a] Bond orders between the metal atoms as high as quadruple may be formed when a high degree of electron density is placed on

the metal centers and the metal valence orbitals can overlap sufficiently. A basic question that we hope to answer by these studies is what are the electronic requirements (limitations) for forming multiple metal–metal bonds. The lack of complexes containing both multiple metal–metal bonds and π-acidic ligands (e.g., CO) shows that these structural components tend to be generally incompatible for reasons that have been discussed.[1b]

With this historical backdrop we were surprised to see a recent report that WBr₂(CO)₄ reacts with diolefins (L-L =

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norbornadiene, cyclooctadiene, cyclooctatetraene) to give dimeric complexes for which two structures were proposed:



The possibility of forming complex **II**, containing both a quadruple bond and $\pi$-acid ligands CO and C=C, was particularly intriguing to us. We decided that an X-ray diffraction study of one of these products was desirable to (1) confirm the existence of a metal–metal bond and (2) determine the order of such a bond. The norbornadiene (NBD) derivative was selected for this study because it was reported to be the most stable.[2] The results obtained on **1** then prompted us to conduct a structural examination of $WBr_2(CO)_2(PPh_3)_2$.

## Experimental Section

All syntheses were conducted on a Schlenk line. Isolated products were stored in a nitrogen-filled drybox or in Schlenk tubes. Methylene chloride was dried by refluxing over $P_2O_5$ under $N_2$. Hexane was dried by refluxing over benzophenone ketyl. $WBr_2(CO)_4$ was synthesized by the method of Bowden and Colton[3] as modified by us.[4] Norbornadiene was stored over molecular sieves before use. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer. $^1H$ NMR spectra were obtained on an EM 390 spectrometer. Visible spectra were recorded on a Cary 17 spectrophotometer.

**Syntheses. $WBr_2(CO)_2C_7H_8$ (1).** $WBr_2(CO)_4$ (1.10 g, 2.41 mmol) was dissolved in $CH_2Cl_2$ (50 mL) in a three-neck flask equipped with a stir bar. The solution was cooled to −78 °C, and a slight excess of norbornadiene (NBD) (0.36 mL, 3.32 mmol) was added via syringe. The solution was allowed to warm to room temperature and stirred for 8 h during which time it acquired a deep wine red color. The solution was concentrated almost to dryness (prolonged drying in vacuo causes decomposition), and 150 mL of a 10:1 hexane:$CH_2Cl_2$ solution was added. The purple solution was separated from some insoluble tan powder by filtration through Celite. The purple filtrate was evaporated just to dryness to give 900 mg (65% yield) of a microcrystalline dark green powder of **1**. Compound **1** may be recrystallized from $CH_2Cl_2$ at −20 °C as purple prisms or from hexane as very thin dark green plates. **1** turns black and loses $CH_2Cl_2$ when exposed to the drying conditions of the drybox. IR ($CH_2Cl_2$) ($cm^{-1}$): 2063 (w), 1992 (s). $^1H$ NMR (90 MHz, CDCl$_3$): δ 5.40 (s, 2 H, $CH_2Cl_2$) 4.50 (t, 4 H), 4.06 (m, 2 H), 0.94 (t, 2H, NBD). FDMS: principal parent $m/e$ peaks at 490, 492, 494; no 2 P, 2 P − CO, etc., peaks observed by this "soft" ionization technique.

**2.** The synthesis of **2** followed essentially the method of Colton and Tomkins.[5] However, we found that 3 days, instead of 3 h, of refluxing in methylene chloride were required to convert $WBr_2$-$(CO)_3(PPh_3)_2$ to **2**. IR ($CH_2Cl_2$) ($cm^{-1}$): 1943 (m), 1857 (s). UV–visible spectra of **1** and **2** were measured on a Cary Model 17 spectrophotometer.

**Collection of Crystallographic Data.** Examination of crystals of **1** under a polarizing microscope revealed their dichroic nature; i.e., as a crystal was rotated through 90° intervals it passed abruptly through red and blue colors. A suitable dark purple prism of **1** recrystallized from methylene chloride was mounted in a capillary sealed with epoxy cement. Reflection data for **1** were collected on an Enraf-Nonius CAD-4 automated diffractometer. General aspects of the data collection and refinement procedures have been described elsewhere.[6] For **1** unit cell dimensions were determined by a least-squares fit to 25 strong reflections in the range 20° ≤ 2θ ≤ 30°. Reflection data were collected in the range 4° ≤ 2θ ≤ 50°. The crystal showed a 3.6% decay in intensity based on three strong reflections over the course of data collection. The data were corrected for this

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**Table I. Crystallographic Parameters**

| parameter | 1 | 2 |
|---|---|---|
| space group | $P2_1/n$ | $P1$ |
| formula | $WBr_2O_2C_9H_8$ | $WBr_2P_2O_2C_{38}H_{30}$ |
| fw | 491.7 | 924.0 |
| $a$, Å | 7.506 (7) | 9.418 (5) |
| $b$, Å | 12.643 (8) | 10.021 (4) |
| $c$, Å | 12.296 (6) | 19.898 (6) |
| $\alpha$, deg | | 90.54 (3) |
| $\beta$, deg | 99.60 (7) | 112.80 (3) |
| $\gamma$, deg | | 92.02 (4) |
| $V$, Å$^3$ | 1150 (2) | 1730 (1) |
| $d$(calcd), g cm$^{-3}$ | 2.832 | 1.772 |
| $Z$ | 4 | 2 |
| cryst size, mm | 0.2 × 0.4 × 0.3 | 0.3 × 0.3 × 0.1 |
| data collecn instrument | CAD-4 | Syntex P1 |
| radiation | Mo Kα | Mo Kα |
| $\mu$(Mo Kα), cm$^{-1}$ | 171.0 | 58.1 |
| range 2θ, deg | 4–50 | 4–50 |
| no. of unique data with $F_o^2 > 3\sigma(F_o^2)$ | 1431 | 1968 |
| no. of variables | 127 | 386 |
| $R_1$ | 0.032 | 0.064 |
| $R_2$ | 0.038 | 0.072 |
| esd | 1.13 | 1.16 |
| largest shift[a] | 0.11 | 0.30 |
| largest peak[b] | 0.75 | 1.9[c] |

[a] Largest parameter shift after final least-squares calculation. [b] Largest peak in final difference Fourier. [c] Ghost located 1.5 Å from W.

decay, and absorption corrections were also applied based on $\psi$ scans of five reflections with Eulerian angle $\chi$ close to 90°. Systematic absences of $h0l$, $h + l \neq 2n$, and for ($0k0$), $k \neq 2n$, indicated that **1** belonged to space group $P2_1/n$. A summary of the data is presented in Table I.

Data for **2** were collected on a Syntex P1̄ diffractometer. Cell dimensions were determined by a least-squares fit to 15 reflections in the range 18° ≤ 2θ ≤ 24°. The crystal showed negligible decay in intensity over the course of data collection. The data were corrected for absorption on the basis of nine reflections with $\chi$ = 90°, or 270 ± 15°. No systematic absences were seen, and all observations were consistent with one of the triclinic space groups $P1$ or $P1̄$. The choice of $P1̄$ was supported by successful refinement.

**Solution and Refinement of Structures.** The positions of the tungsten atoms in **1** and **2** were determined by inspection of three-dimensional Patterson functions. All other non-hydrogen atoms were determined in subsequent difference Fourier syntheses. The structure of **1** was refined by full-matrix least-squares techniques using anisotropic thermal parameters for all atoms. The structure of **2** was refined anisotropically for all atoms except the phenyl carbon atoms, which were refined isotropically. Inspection of a final difference Fourier map of **1** showed no peaks greater than 0.75 e/Å$^3$. Several of the remaining peaks of electron density were located at possible positions for hydrogen atoms. However, attempts to refine these atoms using fixed or varying thermal parameters failed to produce reasonable C–H bond lengths. The final difference map of **2** failed to show any peaks of structural significance. Data collection conditions and final refinement values for **1** and **2** are presented in Table I. Final positional parameters are in Tables II and III. Although $CH_2Cl_2$ was detected in the lattice of **1** by the $^1H$ NMR spectrum of a solution of crystals, the site (or sites) for $CH_2Cl_2$ molecule was apparently only fractionally occupied and sufficiently disordered to prevent recognition of the molecules crystallographically.

**Electronic Structure Calculations.** Calculations of the electronic structures of **1** and **2** have been performed on a VAX 11/780 computer using the Fenske–Hall nonempirical SCF–MO program MEDIEVAL.[7] As is customary for calculations involving W, we have substituted a Slater-type orbital (STO) basis set optimized for Mo. This basis set was composed of optimized linear combinations of four s-type STO's, three p-type STO's, and four d-type STO's. The valence 5s and 5p orbitals were additionally described by a Slater function having $\zeta$ = 2.20. Nonvalence (core) orbitals were frozen for all atoms in

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**Table II.** Positional Parameters and Their Estimated Standard Deviations for $WBr_2(CO)_2(C_7H_8)$ (1)

| atom | $x$ | $y$ | $z$ | $B,^a$ $Å^2$ |
|---|---|---|---|---|
| W(1) | 0.11707 (6) | 0.19194 (4) | 0.29812 (3) | 2.302 (8) |
| Br(2) | 0.5663 (2) | 0.4003 (1) | 0.61628 (9) | 3.82 (3) |
| Br(1) | 0.3925 (2) | 0.1103 (1) | 0.4063 (1) | 4.47 (3) |
| O(1) | −0.119 (1) | 0.0133 (7) | 0.3859 (7) | 5.2 (2) |
| C(1) | −0.037 (2) | 0.077 (1) | 0.3555 (8) | 3.5 (3) |
| O(2) | 0.375 (1) | 0.3457 (8) | 0.1931 (8) | 6.3 (3) |
| C(2) | 0.284 (2) | 0.2908 (9) | 0.233 (1) | 3.6 (3) |
| C(8) | −0.170 (2) | 0.289 (1) | 0.397 (1) | 3.7 (3) |
| C(5) | 0.004 (2) | 0.411 (1) | 0.329 (1) | 3.9 (3) |
| C(3) | 0.026 (2) | 0.2683 (9) | 0.4483 (8) | 3.4 (3) |
| C(7) | −0.165 (1) | 0.2584 (9) | 0.2802 (9) | 3.2 (2) |
| C(6) | −0.060 (2) | 0.331 (1) | 0.2368 (9) | 3.6 (3) |
| C(4) | 0.135 (2) | 0.3405 (9) | 0.4077 (9) | 3.5 (3) |
| C(9) | −0.164 (2) | 0.409 (1) | 0.389 (1) | 4.5 (3) |

$^a$ Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

**Table III.** Positional Parameters and Their Estimated Standard Deviations for $WBr_2(CO)_2(PPh_3)_2$ (2)

| atom | $x$ | $y$ | $z$ | $B,^a$ $Å^2$ |
|---|---|---|---|---|
| W | −0.0018 (2) | 0.1932 (1) | −0.25155 (7) | 2.07 (2) |
| Br(1) | 0.0558 (4) | 0.0015 (3) | −0.3222 (2) | 5.51 (9) |
| Br(2) | −0.0683 (4) | −0.0020 (3) | −0.1845 (2) | 5.38 (9) |
| P(1) | 0.1999 (9) | 0.3043 (8) | 0.8572 (4) | 3.1 (2) |
| P(2) | 0.2013 (9) | 0.7017 (8) | 0.3571 (4) | 3.2 (2) |
| O(1) | 0.192 (2) | 0.371 (2) | 0.684 (1) | 4.9 (6) |
| O(2) | 0.177 (3) | 0.648 (2) | 0.176 (1) | 4.9 (6) |
| C(1) | 0.109 (3) | 0.310 (2) | 0.706 (2) | 3.5 (7) |
| C(2) | 0.113 (3) | 0.701 (3) | 0.207 (1) | 3.6 (8) |
| C(3) | 0.379 (3) | 0.205 (3) | 0.881 (2) | 3.8 (7) |
| C(4) | 0.470 (4) | 0.216 (3) | 0.958 (2) | 7 (1) |
| C(5) | 0.381 (4) | 0.858 (4) | 0.017 (2) | 8 (1) |
| C(6) | 0.334 (4) | 0.903 (4) | 0.068 (2) | 7 (1) |
| C(7) | 0.423 (4) | 0.910 (4) | 0.144 (2) | 9 (1) |
| C(8) | 0.435 (4) | 0.152 (3) | 0.836 (2) | 7 (1) |
| C(9) | 0.255 (4) | 0.477 (3) | 0.840 (2) | 4.4 (8) |
| C(10) | 0.407 (4) | 0.512 (3) | 0.855 (2) | 5 (1) |
| C(11) | 0.453 (4) | 0.646 (4) | 0.846 (2) | 7 (1) |
| C(12) | 0.330 (4) | 0.736 (3) | 0.822 (2) | 6 (1) |
| C(13) | 0.179 (4) | 0.701 (3) | 0.811 (2) | 5 (1) |
| C(14) | 0.146 (3) | 0.568 (3) | 0.823 (2) | 4.2 (8) |
| C(15) | 0.176 (3) | 0.325 (3) | 0.945 (1) | 3.2 (7) |
| C(16) | 0.204 (4) | 0.446 (3) | 0.983 (2) | 4.8 (9) |
| C(17) | 0.179 (4) | 0.448 (4) | −0.951 (2) | 6 (1) |
| C(18) | 0.123 (4) | 0.345 (3) | 0.073 (2) | 5.6 (9) |
| C(19) | 0.097 (4) | 0.225 (4) | 0.034 (2) | 6 (1) |
| C(20) | 0.123 (4) | 0.217 (4) | −1.033 (1) | 5 (1) |
| C(21) | 0.168 (3) | 0.670 (3) | 0.440 (2) | 3.4 (8) |
| C(22) | 0.236 (4) | 0.563 (3) | 0.483 (2) | 4.6 (9) |
| C(23) | 0.214 (4) | 0.550 (4) | 0.551 (1) | 4.9 (9) |
| C(24) | 0.124 (4) | 0.646 (4) | 0.575 (2) | 6 (1) |
| C(25) | 0.073 (4) | 0.738 (4) | 0.531 (2) | 6 (1) |
| C(26) | 0.077 (4) | 0.760 (3) | 0.462 (2) | 4.7 (9) |
| C(27) | 0.383 (3) | 0.803 (2) | 0.387 (1) | 2.8 (6) |
| C(28) | 0.489 (4) | 0.802 (4) | 0.466 (2) | 7 (1) |
| C(29) | 0.358 (4) | 0.135 (4) | 0.512 (2) | 7 (1) |
| C(30) | 0.327 (4) | 0.059 (4) | 0.559 (2) | 7 (1) |
| C(31) | 0.436 (5) | 0.057 (4) | 0.635 (2) | 8 (1) |
| C(32) | 0.418 (4) | 0.876 (3) | 0.339 (2) | 7.7 (9) |
| C(33) | 0.261 (3) | 0.537 (3) | 0.339 (1) | 3.3 (8) |
| C(34) | 0.168 (4) | 0.431 (3) | 0.331 (1) | 4.3 (9) |
| C(35) | 0.216 (5) | 0.310 (3) | 0.313 (2) | 7 (1) |
| C(36) | 0.355 (4) | 0.290 (3) | 0.302 (2) | 6 (1) |
| C(37) | 0.445 (4) | 0.404 (3) | 0.312 (2) | 6 (1) |
| C(38) | 0.403 (4) | 0.535 (4) | 0.327 (2) | 7 (1) |

$^a$ Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

the SCF procedure. Calculations were performed on the molecules with essentially the same geometries as determined by X-ray diffraction. The norbornadiene ligand of 1 was replaced by two ethylene molecules. The CO ligands were idealized to a perfectly *trans*
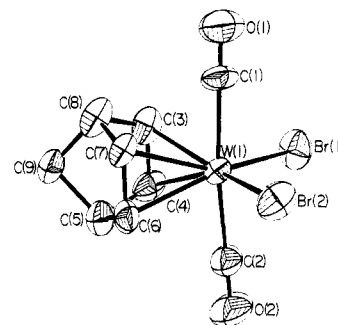


**Figure 1.** Molecular structure of $WBr_2(CO)_2C_7H_8$ (1). Each atom is represented by its ellipsoid of thermal vibration at the 40% probability level.

**Table IV.** Bond Lengths (Å) and Selected Bond Angles (deg) in $WBr_2(CO)_2(C_7H_8)$ (1)

| Bond Lengths | | | |
|---|---|---|---|
| W–Br(1) | 2.489 (1) | C(1)–O(1) | 1.12 (1) |
| –Br(2) | 2.493 (1) | C(2)–O(2) | 1.14 (1) |
| –C(1) | 2.05 (1) | C(3)–C(8) | 1.52 (2) |
| –C(2) | 2.03 (1) | C(7)–C(8) | 1.49 (2) |
| –C(3) | 2.29 (1) | C(4)–C(5) | 1.54 (2) |
| –C(4) | 2.30 (1) | C(6)–C(5) | 1.53 (2) |
| –C(6) | 2.26 (1) | C(5)–C(9) | 1.57 (2) |
| –C(7) | 2.26 (1) | C(8)–C(9) | 1.53 (2) |
| | | C(3)–C(4) | 1.38 (2) |
| | | C(6)–C(7) | 1.38 (2) |

| Bond Angles | | | |
|---|---|---|---|
| Br(1)–W–Br(2) | 105.86 (5) | Br(2)–W–C(6) | 94.2 (3) |
| C(1)–W–C(2) | 172.9 (4) | –C(7) | 94.9 (3) |
| Br(1)–W–C(1) | 89.3 (3) | –C(3) | 154.1 (3) |
| –C(2) | 87.4 (4) | –C(4) | 153.1 (3) |
| Br(2)–W–C(1) | 88.0 (3) | W–C(1)–O(1) | 179 (1) |
| –C(2) | 86.9 (3) | W–C(2)–O(2) | 178 (1) |
| Br(1)–W–C(3) | 94.5 (3) | C(3)–W–C(7) | 61.3 (4) |
| –C(4) | 93.6 (3) | C(4)–W–C(6) | 62.1 (4) |
| –C(6) | 153.1 (3) | C(3)–W–C(4) | 34.9 (3) |
| –C(7) | 152.9 (3) | C(6)–W–C(7) | 35.5 (4) |

alignment. The PPh$_3$ ligands of **2** were substituted by PH$_3$, r(P–H) = 1.35 Å, and the dihedral angle (22°) between the Br–W–Br and OC–W–CO planes was flattened to 0° to permit a discussion in terms of full $C_{2v}$ symmetry. All calculations were carried out in a right-handed coordinate system, with the z axis bisecting the Br–W–Br angle. To aid in the interpretation of the results, the orbitals obtained were transformed to a basis composed of free-ligand orbitals.

## Results and Discussion

**Reaction Product of WBr$_2$(CO)$_4$ with Norbornadiene.** The reaction was carried out in an effort to reproduce the product briefly described by Davidson and Vasapolla,[2] and we believe that our product and theirs are the same (vide infra). Purple crystals of this compound were obtained from methylene chloride solution, and from an X-ray crystallographic study, the compound was shown to be WBr$_2$(CO)$_2$(NBD), where NBD represents norbornadiene. The structure of the molecule is shown in Figure 1. No crystallographic symmetry is imposed on the molecule, but it comes close to having $C_{2v}$ symmetry. Table IV lists the bond lengths and angles that are pertinent to the discussion, and it can be seen that deviations from $C_{2v}$ symmetry, while statistically real, are small. Presumably they would not persist in the free molecule.

While the molecule might be qualitatively described as octahedral, there are some sizeable deviations from that idealized arrangement. The Br–W–Br angle is ca. 106°, whereas the angle subtended at the tungsten atom by the midpoints of the carbon–carbon double bonds is only 62.8°. The *trans*-W(CO)$_2$ unit is also slightly bent at the metal atom, the C–W–C angle being 172.9°.

The infrared and $^1$H NMR spectra of **1** are virtually identical with those reported by Davidson and Vasapollo for

their compound.[2] The infrared spectrum of this complex deserves some comment. The carbonyl bands in the infrared spectrum of **1** in methylene chloride solution are fully consistent with the trans configuration observed crystallographically—the higher energy band at 2063 cm$^{-1}$ is due to the symmetric stretching mode and the band at 1992 cm$^{-1}$ is due to the antisymmetric mode. Indeed, considering the large coupling between these two modes ($\Delta\nu = 71$ cm$^{-1}$), it would be surprising if any complex containing chemically equivalent carbonyls on *different* metal centers could produce such a spectrum.

Surprisingly, the infrared spectrum of **1** in hexane is more complex and contains four carbonyl stretching bands, at 2065 (w), 2008 (s), 1985 (m), and 1975 (m) cm$^{-1}$. This may be attributable to association, probably dimerization, whereby the electronic unsaturation of the tungsten atoms is relieved by the formation of bromine bridges. The colors of the CH$_2$Cl$_2$ and hexane solutions are both purple, however. On the other hand, crystals of **1** differ in color as well as habit depending upon the crystallization solvent. Those from methylene chloride are (like the solution in that solvent) also purple. They are prismatic in habit, and one of these served well for the structure determination reported here. On the other hand crystals obtained from the purple hexane solution are green and in the form of very thin plates. Unfortunately, they are too thin for X-ray crystallography. It is possible that they may contain the binuclear molecules with seven-coordinate metal atoms mentioned above in connection with the IR spectrum in hexane. Thus, while we think it may be that dimeric molecules of **1** occur in either solid or solution, or both, we do not think it likely that they are of the previously suggested[2] types, I or II. In any event, these structures are deficient in CO as compared to a dimer of **1**.

Davidson and Vasapollo[1] also had some mass spectral evidence to support dimers of the types I and II, and we therefore considered it pertinent to examine **1** by mass spectrometry. Three techniques were used: (1) field desorption (FD); (2) fast atom bombardment (FAB); (3) electron impact (EI). The "soft" FD technique gave only the spectrum of the parent ion of **1**. No higher (or lower) mass species were detected by this technique. The "hard" FAB and EI techniques gave completely different results. Now, the parent ion peaks were completely absent, and the spectra were not readily interpretable. While some higher mass peaks were observed by these hard techniques, their signal-to-noise ratio is very poor and only masses as high as those expected for P + CO and P + 2 CO are detectable. In short, the mass spectral results obtained are quite dependent on the technique employed, and we have been unable to find conditions under which we could reproduce the previously reported results.

Peaks consistent with structures I or II would presumably result only if the coupling of two molecules of **1** were accompanied (not necessarily simultaneously) by the loss of two molecules of CO. It is not evident what conditions would favor such a process.

One aspect of the reaction chemistry of **1** was examined. Addition of an excess of PMe$_2$Ph to **1** in chloroform resulted in displacement of the NBD ligand and led to the isolation of WBr$_2$(CO)$_2$(PMe$_2$Ph)$_3$. This result agrees with that reported by Davidson and Vasapollo. When a trace of PMe$_2$Ph was added to a CDCl$_3$ solution of **1** in an NMR tube, the solution turned orange and the NBD resonances cleanly moved to higher field, indicating that both NBD and PMe$_2$Ph are coordinated to W. The new set of NBD resonances ($\delta$ 4.10 t, 4 H), 3.67 (m, 2 H), 1.45 (s, 2 H)) were in very close agreement with those reported by Davidson for his orange product formulated as WBr$_2$(CO)(PMe$_2$Ph)(NBD). No gas evolution was apparent in this reaction, and we believe a more
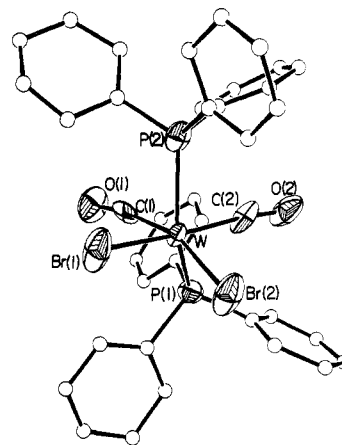


**Figure 2.** Molecular structure of WBr$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**). The phenyl carbon atoms are represented by circles of arbitrary size, while the other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

**Table V.** Selected Bond Lengths (Å) and Bond Angles (deg) in WBr$_2$(CO)$_2$(PPh$_3$)$_2$ (**2**)

| Bond Lengths | | | |
|---|---|---|---|
| W–Br(1) | 2.565 (3) | W–C(2) | 1.94 (4) |
| W–Br(2) | 2.571 (4) | C(1)–O(1) | 1.18 (3) |
| W–P(1) | 2.481 (9) | C(2)–O(2) | 1.16 (3) |
| W–P(2) | 2.486 (9) | P–C(av) | 1.85 [1] |
| W–C(1) | 1.95 (4) | | |

| Bond Angles | | | |
|---|---|---|---|
| Br(1)–W–Br(2) | 82.0 (1) | Br(2)–W–C(1) | 161.5 (8) |
| P(1)–W–P(2) | 128.3 (3) | –C(2) | 84.6 (9) |
| C(1)–W–C(2) | 110 (1) | P(1)–W–C(1) | 77 (1) |
| Br(1)–W–P(1) | 122.3 (2) | –C(2) | 75 (1) |
| –P(2) | 97.7 (2) | P(2)–W–C(1) | 74 (1) |
| Br(2)–W–P(1) | 96.8 (2) | –C(2) | 76 (1) |
| –P(2) | 121.9 (2) | W–C(1)–O(1) | 172 (3) |
| Br(1)–W–C(1) | 86.7 (8) | W–C(2)–O(2) | 173 (3) |
| –C(2) | 159.4 (9) | | |

likely formula for this complex is the 18-electron adduct of **1**, WBr$_2$(CO)$_2$(NBD)(PMe$_2$Ph). We have not examined the reaction chemistry of **1** in any other way.

**WBr$_2$(CO)$_2$(PPh$_3$)$_2$ (2).** The immediate product of reacting triphenylphosphine with WBr$_2$(CO)$_4$ is the 7-coordinate, 18-electron species WBr$_2$(CO)$_3$(PPh$_3$)$_2$. The 16-electron compound is obtained by heating this initial product in refluxing methylene chloride for 3 days, whereby 1 mol of CO is expelled. The greater difficulty in reducing the number of carbonyl groups from three to two in this case, as compared to the norbornadiene compound, despite the much greater steric factor for the PPh$_3$ ligands, presumably shows that the two phosphine ligands leave more metal d$\pi$ electron density for back-bonding to CO groups than do the two olefin groups from the NBD. In support of this, we find that the CO stretching frequencies in **2** (1943 (m), 1857 (s) cm$^{-1}$) are much lower than those in **1** (2063 (w), 1992 (s) cm$^{-1}$). Compound **2** readily adds CO to regenerate the tricarbonyl.[8] A single-crystal X-ray diffraction study on **2** reveals it to have the structure depicted in Figure 2. The important bond distances and angles are listed in Table V. The molecule is highly distorted from octahedral geometry with a P–W–P angle of 128.3 (3)°, a C–W–C angle of 110 (1)°, and a Br–W–Br angle of 82.0 (1)°. Furthermore, the Br–W–Br plane makes a 22°

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(8) We have observed similar behavior for **1**. Upon treatment of **1** in methylene chloride with 1 atm of CO a black precipitate and a colorless solution result. Removal of the CO under vacuum restores the purple solution of **1**. However, this process is not fully reversible. Not all of the black material redissolves, and this cycle may be repeated only twice more before decomposition is complete.

**Table VI.** Some Molecular Orbitals Near the HOMO-LUMO Gap in $MoBr_2(CO)_2(PH_3)_2$ according to a Fenske-Hall Calculation

| orbital | $E$, eV | Mo | Br | CO ($\pi^*$) | PH$_3$ |
|---------|---------|-----|----|--------------|--------|
| 2a$_1$ | 3.89 | 30 ($z^2$) | 5 | 61 | |
| 2a$_2$ | 3.16 | 26 ($xy$) | | 73 | |
| 2b$_1$ | 2.20 | | | 92 | 6 |
| 2b$_2$ | -0.55 | | 8 | 85 | |
| 1b$_1$ | -3.91 | 69 ($xz$), 14 ($x$) | 7 | | 9 |
| 1a$_2$ | -7.32 | 45 ($xy$) | 35 | 18 | |
| 1a$_1$ | -7.35 | 45 ($z^2$) | 30 | 22 | |

$^a$ Those <5% are not listed.

**Table VII.** Some Molecular Orbitals Near the HOMO-LUMO Gap in $MoBr_2(CO)_2(C_2H_4)_2$ according to a Fenske-Hall Calculation

| orbital | $E$, eV | Mo | Br | CO ($\pi^*$) | C$_2$H$_4$ ($\pi^*$) |
|---------|---------|-----|----|--------------|----------------------|
| 3b$_2$ | 3.48 | 63 ($yz$) | 14 | | 16 |
| 3b$_1$ | 2.54 | 20 ($xz$) | | | 74 |
| 2b$_1$ | 2.43 | 15 ($xz$) | | 83 | |
| 3a$_2$ | 2.41 | 18 ($xy$) | | 82 | |
| 2a$_1$ | -0.08 | | | 91 | |
| 2a$_2$ | -0.13 | 21 ($xy$) | | | 77 |
| 2b$_2$ | -0.62 | | | 92 | |
| 1a$_1$ | -6.66 | 57 ($z^2$), 16 ($x^2 - y^2$) | 18 | | |
| 1a$_2$ | -10.05 | 25 ($xy$) | 53 | 6 | 14 |
| 1b$_1$ | -10.05 | 33 ($xz$) | 43 | 7 | 13 |

$^a$ Those under 5% omitted.

dihedral angle with the C-W-C plane. The overall structure of **2** is quite similar to that reported for the molybdenum analogue.[9] However, refinement difficulties, presumably due to disorder, were encountered with the latter compound (leading to final $R_1$ and $R_2$ values of 0.15 and 0.11, respectively). Compound **2** also is diamagnetic as judged by its $^1$H NMR spectrum.

**Electronic Structure and Spectra. $M_2X_2(CO)_2(PR_3)_2$ Compounds.** We begin with this case since it is more familiar and has already been discussed by Kubáček and Hoffmann (KH).[10] KH gave a qualitative discussion and also attempted to calculate the preferred molecular shape by using the extended Hückel (EH) method. We fully subscribe to KH's arguments because of the logic on which they are based. In addition, our Fenske-Hall (FH) calculations give a pattern of orbital energies that is fully in accord with their qualitative picture. In our calculation we have idealized the structure to $C_{2v}$ symmetry. The principal way in which this deviates from the actual structure is in having the $MX_2(CO)_2$ set of atoms strictly coplanar rather than allowing a dihedral angle to exist between the $MX_2$ and $M(CO)_2$ planes. We have also used a Cartesian coordinate system that is natural to this symmetry, namely one in which the $z$ axis corresponds to the $C_2$ symmetry axis (and thus bisects the X-M-X and C-M-C angles). The $y$ axis was chosen to be in the $MX_2(CO)$ plane and the $x$ axis perpendicular to it. That used by KH, which was more convenient for their qualitative discussion, is different.

The results of our FH calculation for the model compound $MoBr_2(CO)_2(PH_3)_2$, using the experimentally determined bond lengths and angles for $WBr_2(CO)_2(PPh_3)_2$ (which are not significantly different from those for $MoBr_2(CO)_2(PPh_3)_2$), are listed, in part, in Table VI. Further results are available in the supplementary material. The three lowest lying orbitals of predominantly metal d character are 1a$_1$ ($z^2$), 1a$_2$ ($xy$), and 1b$_1$ ($xz$). The first two, which have the same energy within the error limits of the calculation, are filled by the four d electrons; the 1b$_1$ orbital lies about 3.4 eV higher and is empty. The lack of unpaired electrons in this "octahedral" d$^4$ complex is thus nicely accounted for.

Our results are qualitatively in complete accord with those of KH, although the comparison is a little tedious because of the different choices of Cartesian coordinates. KH propose that orbitals of (in their coordinate system) $x^2 - y^2$ and $yz$ character are occupied while the lowest unoccupied d orbital is d$_{xz}$. Their $yz$ orbital corresponds directly to our $xy$ orbital while their $x^2 - y^2$ orbital corresponds partially to our $z^2$ orbital. Thus, the two occupied orbitals are essentially the same according to both analyses. Similarly, their lowest unoccupied orbital, $xz$, corresponds directly to our lowest unoccupied orbital, which also happens to be designated $xz$. It can also be seen in Table VI that the next four unoccupied MO's are

those that are essentially CO $\pi^*$ in character.

Another interesting point to note about the orbital splitting pattern in the $MX_2(CO)_2(PR_3)_2$ type molecule is that the strong distortion from octahedral symmetry is of paramount importance in producing the large HOMO-LUMO gap (ca. 3 eV) that assures a spin-paired ground state. We make this point here because it differentiates this case from that of $WBr_2(CO)_2(C_7H_8)$, to be discussed next, where distortions are small and are *not* necessary to achieve the spin-paired ground state. A calculation of $MoBr_2(CO)_2(PH_3)_2$ was also done in which the P-Mo-P angle was kept at 180°. In this case the 1b$_1$ orbital lies only 0.5 eV above the virtually degenerate pair, 1a$_1$ and 1a$_2$. With such a small spacing, it would be very likely that a triplet ground state would occur. The bending of the P-Mo-P angle increases the energy of the 1b$_1$ orbital, and the four electrons are thus forced to occupy the lower two.

To look at the system in this way is to invoke, in essence, a second-order Jahn-Teller effect. We think that this point of view is an entirely valid one, and we must, therefore, disagree somewhat with KH's position when they noted "with disappointment, the relative *inutility* of...Jahn-Teller arguments...in guiding us to geometrical predictions in these molecules".

**Bonding in $MX_2(CO)_2$(diene) Molecules.** An understanding of the orbital splitting pattern in this type of molecule (which has not been discussed previously) is obtainable by neat, simple arguments that do *not* depend upon invoking distortions from octahedral angles about the metal atom. Let us begin with a purely qualitative analysis, in which we chose Cartesian axes so that the $z$ axis coincides with the OC-M-CO direction and the $x$ and $y$ axes lie along the M-Br bonds.

We first allow for the major splitting of the metal d-orbital manifold into the $\sigma^*(e_g)$ pair and the $\pi(t_{2g})$ triplet. We then ask what splitting of the $\pi$ triplet would be expected as a result of metal-ligand $\pi$ interactions. The $\pi$ interactions of the bromine ligands will be of secondary importance; the $\pi$ interactions involving the CO and olefin ligands will dominate, and these cooperate to favor the same splitting pattern. Clearly, in the coordinate system we have adopted, the usual interaction between $\pi^*$ orbitals of the CO groups and the set of d$\pi$ orbitals of the metal atom will lower the energies of the d$_{xz}$ and d$_{yz}$ orbitals while leaving the d$_{xy}$ orbital unaffected. The $\pi^*$ orbitals of the two olefinic moieties in the norbornadiene ligand also will interact with and depress only the d$_{xz}$ and d$_{yz}$ orbitals, again leaving the d$_{xy}$ orbital unaffected. Thus, a clear qualitative prediction can be made that the d$\pi$ manifold is split into a lower d$_{xz}$,d$_{yz}$ pair and an upper d$_{xy}$ orbital. Moreover, in view of the cooperativity of the influences from both the CO groups and the olefin ligands, we might well expect this splitting to be large enough to assure that there is a singlet ground state based on a d$_{xz}^2$d$_{yz}^2$d$_{xy}^0$ electronic configuration.

To provide some semiquantitative support for the preceding

(9) Drew, M. G. B.; Tomkins, I. B.; Colton, R. *Aust. J. Chem.* **1970**, *23*, 2517. Note that the C-Mo-C angle is erroneously given as 119.4° whereas it is actually close to 110°, as we find in the tungsten analogue.

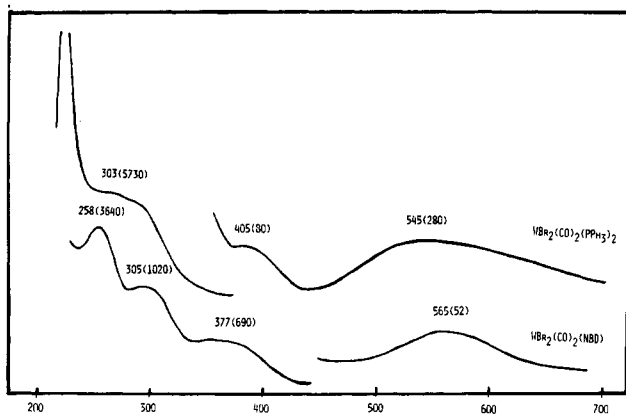(10) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

**Figure 3.** Visible absorption spectra of compounds **1** (lower) and **2** (upper). The wavelength scale is in nanometers, and all absorption maxima are marked with their exact wavelengths and, in parentheses, their molar extinction coefficients.

qualitative discussion, we have carried out a Fenske–Hall calculation using $MoBr_2(CO)_2(H_2C=CH_2)_2$ as a model compound. The model was designed to have perfect $C_{2v}$ symmetry with the interatomic distances and angles set equal to the mean values of those found in $WBr_2(CO)_2(C_7H_8)$, except that the angle subtended at the metal atom by the midpoints of the C=C bonds was set at exactly 90°. The planar $H_2C=CH_2$ molecules were set precisely perpendicular to the lines from the Mo atom to the midpoints of the C=C bonds. The coordinate axes were chosen with the $z$ axis corresponding to the $C_2$ axis of symmetry (i.e., bisecting the Br–Mo–Br angle) and the $x$ axis coinciding with a strictly linear OC–Mo–CO chain of atoms.

The results of the FH calculation are summarized in Table VII. A figure showing more of the results, including those for various fragments, is available as supplementary material. These results fully confirm the qualitative analysis. The metal $d\pi$ type orbitals are grouped into a pair of virtually the same energy, $1b_1$ ($xz$) and $1a_2$ ($xy$), which are filled, and some 3.3 eV higher in energy, the empty $1a_1$ ($z^2$) orbital.

**Electronic Absorption Spectra.** The electronic absorption spectra of both compounds are shown in Figure 3. In each case there is a broad absorption band in the 500–600-nm region. We believe that these bands can be attributed to the transitions from the two highest filled $d\pi$ type orbitals to the lowest unfilled orbital, which is also of $d\pi$ character. The calculations in both cases predict the relevant orbital energy differences to be a little over 3 eV whereas the absorption bands are at about 2 eV. Since FH calculations are known to place virtual orbitals at energies that are too high, the predicted and observed energies are in fair agreement. The transitions involved, two of very similar energy in each case, are all dipole allowed in $C_{2v}$ symmetry. However, to the extent that they retain essentially d → d character, they have a parity-forbidden character. This would explain why their intensities are relatively low.

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# Synthesis and Characterization of an Unusual Asymmetric Diosmium Complex, Os₂Cl₃(PhNpy)₃

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The title compound was obtained by reaction of $Os_2(O_2CCH_3)_4Cl_2$ with the ligand 2-anilinopyridine in a toluene solution containing trimethylsilyl chloride. The dark blue crystals formed on addition of hexane and subsequent cooling belong to the triclinic system, space group $P\bar{1}$, with unit cell dimensions of $a$ = 9.269 (3) Å, $b$ = 12.023 (2) Å, $c$ = 16.191 (4) Å, $\alpha$ = 90.84 (2)°, $\beta$ = 100.73 (2)°, $\gamma$ = 97.01 (2)°, and $V$ = 1758 (1) Å³ with $Z$ = 2. The structure was refined to $R$ = 0.035 ($R_w$ = 0.047). The complex is unusual in that each osmium atom is in a different environment. The Os–Os distance, 2.392 (1) Å, is the longest yet recorded for a diosmium complex nominally containing a triple bond. The complex is paramagnetic exhibiting a moment of 1.46 $\mu_B$/Os at 308 K. A dichloromethane solution of the complex displays two distinct absorption bands at 868 ($\epsilon$ = 1880) and 615 nm (4920) in its electronic spectrum and exhibits both oxidative (+0.75 V) and reductive (–0.23, –0.37, –1.25, –1.47 V) waves when examined by cyclic voltammetry.

## Introduction

Although the field of multiply bonded diosmium complexes is a rapidly expanding one, our knowledge of these systems is still very limited.[1] Several complexes of general formula $Os_2(XYZ)_4Cl_2$, where XYZ is a three-atom bridging ligand, have been reported, but the chemistry of these has not as yet been developed in any systematic manner. Complexes are known with the donor sets O,O;[2–5] O,N;[6,7] and P,C.[8] We now report for the first time a triply bonded diosmium complex

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